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# Validity of theoretical models in estimating the sound velocity in toluene-alcohol mixtures

Palaniappan Lakshmanan

School of Physics, Universiti Sains Malaysia, Pualu Penang 11800, Malaysia

E mail lp_dde au@yahoo com

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**Abstract** : Four different theoretical models have been applied to evaluate the sound velocity values at 303 K for the systems studied in our previous work and they are compared with the experimental values. The validity of the Nomoto's relation, the ideal mixing relation, the free length theory and the Rao's specific velocity method is checked and a comparative study of the above models is made. The least square linear fitting equations are generated for additional confirmation. The non-ideal behaviour of the systems is explained in terms of molecular interactions of the constituents of the mixture

**Keywords** . Sound velocity, theoretical models, molecular interactions

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## 1. Introduction

The assessment of the nature of molecular interaction present in materials can be done by ultrasonic investigation. The departure from linearity in the values of sound velocity in liquid mixtures when studied as a function of concentration is found to exhibit interesting variations [1,2]. Of course, the acoustical and thermodynamical properties evaluated in the liquid mixtures signify the physico-chemical and molecular interactions that exist between the components of the system, an additional confirmation for the presence of specific interaction can be made using the estimated sound velocity values. Sound velocity data for three binary mixtures of toluene + aliphatic alcohols were reported in our earlier work [3] and the results were confirmed from the trend of thermo acoustical parameters. An attempt has been made in this paper to correlate the findings of experimental velocity obtained in the cited work with those predicted theoretically that are based on molecular models. Such comparisons are found to be useful in knowing the thermodynamics of the

mixtures and also provide a better means to test the validity of the various empirical and semi empirical theories [4,5] In recent years, various theories [6,7,8] have been in use for computing ultrasonic velocity in liquid mixtures and the deviation in theoretical sound velocity has been attributed mainly to the molecular interactions in the mixtures

Alcohols, in particular methanol and ethanol, are found to posses the ability of azeotrope formation with toluene [9] As such all the azeotropes are non-ideal Further, for a satisfactory degree of separation, all the components of the mixture should show non-ideality Apart from various experimental methods for estimating non-ideality of the liquid mixtures, many theoretical models are also available to do this The estimation of sound velocity and comparing them with the experimental sound velocity is one among the many techniques of the theoretical models Among the various models available for the estimation of sound velocity in the mixtures having non-ideal components, few of them are considered here Thus the present work aims at estimating the sound velocity values at 303 K for the binary mixtures of toluene with methanol, ethanol and 1-propanol and comparing with those of the reported experimental values

## 2. Theoretical aspects

The theoretical models include Nomoto's relation (NR) [10], ideal mixing relation (IMR) [11], free length theory (FLT) [12] and Rao's specific velocity method (Rao) [13] Further the percentage deviation, the molecular interaction parameter, the Chi-square test values and the linear fitting parameters were calculated for a reliable comparison The comparison yields the validity of the theory for these particular systems and also confirms the non-ideality of the systems The least square linear fitting is applicable for systems with weak interactions Of course, here it is taken with a view that the deviations can be attributed to the extent of the non-ideality existing in the systems which will offer additional confirmation

Four theories as cited earlier are considered and their brief description is given hereunder

### *2 1 Nomoto's relation (NR)*

Nomoto established an empirical formula for ultrasonic velocity in binary liquid mixtures with components 1 and 2 on the assumption of linear dependence of the molar sound velocity on concentration in mole fraction and the additivity for molar volume as,

$$U_{NR} = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \tag{1}$$

where $x$ is the mole fraction of the component, $R_1$, $R_2$ the respective molar sound velocities and $V_1$, $V_2$ the molar volumes respectively The molar sound velocity is related to molecular

weight ($m$) and density ($\rho$) as,

$$R = \frac{m}{\rho} U^{1/3} = VU^{1/3} \tag{2}$$

where the molar volume obeys the additivity

$$V = x_1 V_1 + x_2 V_2 \tag{3}$$

*2 2 Ideal Mixture Relation (IMR)*

Van Deal and Vangeal assumed the adiabatic compressibility ($\beta$) of the binary mixture in terms of mole fraction as,

$$\beta_{IM} = x_1 \beta_1 + x_2 \beta_2 \tag{4}$$

On the basis of this equation, the sound velocity is given as,

$$U_{IMR} = \left( \frac{1}{x_1 m_1 + x_2 m_2} \right)^{1/2} \left( \frac{x_1}{m_1 U_1^2} + \frac{x_2}{m_2 U_2^2} \right)^{1/2} \tag{5}$$

*2 3 Free length theory (FLT)*

Jacobson introduced the concept of intermolecular free length to determine the ultrasonic velocity in pure liquids and liquid mixture Further, he related the velocity of the pure liquids to the free length $L_f$ by the equation,

$$U L_f \rho^{1/2} = K_T \tag{6}$$

where $K_T$ is the temperature dependent Jacobson's constant which takes a value of 199 53 $\times 10^{-8}$ in M K S units at 303 K For liquid mixtures, the above equation can be written as,

$$U_{FLT} = \frac{K_T}{L_{f_{mix}} \rho^{1/2}} \tag{7}$$

where $L_{f_{mix}}$ and $\rho$ represents the free length and density of the mixture The free length $L_{f_{mix}}$ of the liquid mixtures is given by,

$$L_{f_{mix}} = 2 \left\{ \frac{\left[ V_{mix} - (x_1 V_{01} + x_2 V_{02}) \right]}{(x_1 Y_1 + x_2 Y_2)} \right\} \tag{8}$$

where $V_{01}$ and $V_{02}$ represent the volume $\left[V_0=V_m U_{expt}/U_\alpha\right]$ of the pure components at absolute zero, $U\alpha$ = 1800 $ms^{-1}$ and

$$Y=\left(\frac{2V_m}{L_{f_{mix}}}\right)\left(1-\frac{U_{expt}}{U_\alpha}\right) \tag{9}$$

is the surface area per mole

*2 4 Rao's specific velocity relation (RAO)*

According to this method,

$$U_{RAO}=\left(\sum x_i r_i \times \rho_{expt}\right)^3 \tag{10}$$

$$r_i=\frac{U_i^{1/3}}{\rho_i} \tag{11}$$

where $r$ is the Rao's specific sound velocity, $\rho_{expt}$ is the experimental density and $\rho_i$ is the density of the $i$-th component

The results obtained using the theoretical models are compared and validated with the experimental values using the respective molecular interaction parameter, percentage deviation, the Chi-square test and the linear least square fit

*2 5 Molecular interaction parameter*

The degree of molecular interaction $\alpha$ is given as,

$$\alpha=\left(\frac{U^2_{expt}}{U^2_{the}}\right)-1 \tag{12}$$

where $U_{expt}$ is the experimental sound velocity and $U_{the}$ is the relevant estimated sound velocity

*2 6 Percentage deviation*

The percentage deviation in sound velocity between the experimental ($U_{expt}$) and computed ($U_{the}$) values are calculated as,

$$\left(\frac{\Delta U}{U}\right)\%=\left(\frac{U_{expt}-U_{the}}{U_{expt}}\right)100\% \tag{13}$$

### *2 7 Chi-Square test for goodness of fit*

The Pearson [14] test of goodness fit is a very powerful tool to determine whether the deviations of the theoretical values from the experimental ones are due to chance or really due to the inadequacy of the theory to fit in the data If $O_i$ ($i$ = 1, 2, 3 $n$) is a set of observed or experimental frequencies and $E_i$ ($i$ = 1, 2, 3 $n$) is the corresponding set of expected or theoretical frequencies, then the Chi-square is given by

$$\text{Chi-Square } (\chi)^2 = \sum_{i=1}^{n}\left[\frac{(O_i - E_i)^2}{E_i}\right] \tag{14}$$

## 3. Experiment

The mixtures of various concentrations in mole fraction were prepared by taking purified AR grade samples (Aldrich make) at 303 K The ultrasonic velocities in liquid mixtures have been measured using the pulse-echo type ultrasound imaging system (USM-25, Krautkramer, Germany) with an overall accuracy of ± 0 1 $ms^{-1}$ The instrument is calibrated with known material velocity and a probe delay of 233 ms is obtained for excellent overlapping of echoes The experiment is performed with the frequency range of 2 to 20 MHz and measurement range of up to 100 mm The experimental temperature is maintained at 303 K by using a thermostat (Krautkramer, Germany) with an accuracy of ± 0 01 K

## 4. Results and discussion

Figures 1–3 shows the trend of the experimental velocity (EXPT) and the various theoretical velocity values obtained for the binary systems of toluene + methanol ethanol and 1-

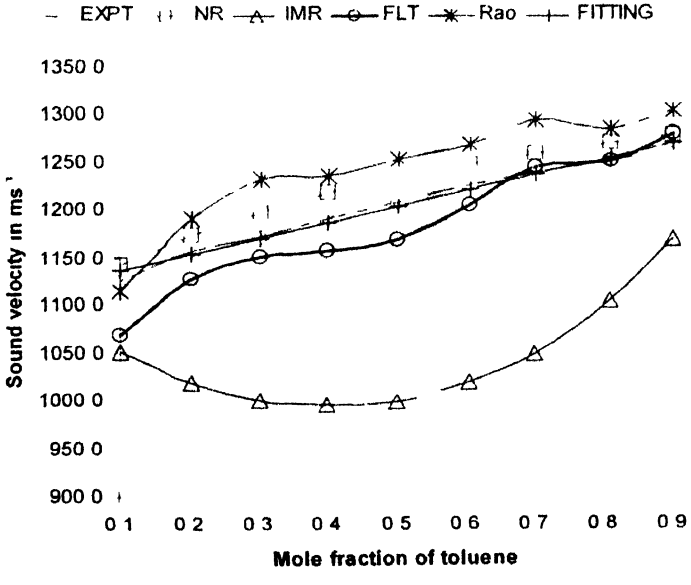


**Figure 1** Trend of sound velocity in methanol system

propanol at 303 K respectively The trend of respective molecular interaction parameters are shown in Figures 4–6 The experimental sound velocity values were fitted to a straight

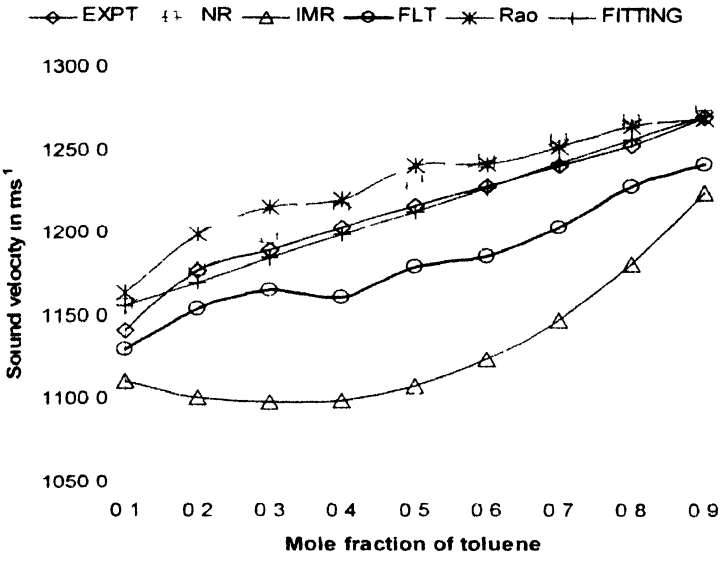


**Figure 2.** Trend of sound velocity in ethanol system

line equation by the unweighted least squares method using Marquardts algorithm The generated fitting equations for the experimental sound velocity along with the standard deviation ($\sigma$) and the correlation coefficient ($R$) are given in Table 1 The respective

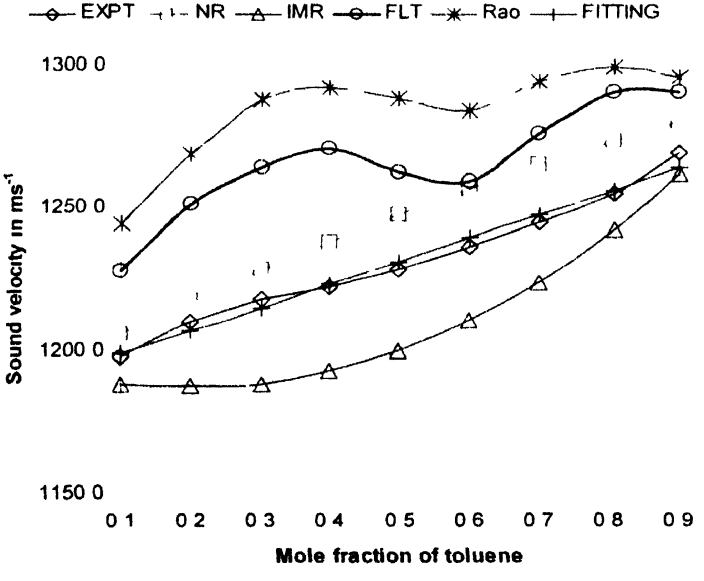


**Figure 3.** Trend of sound velocity in 1-propanol system

percentage deviation of ultrasonic velocity along with Chi-square deviation values are given in Table 2

**Table 1.** Linear fitting equations and parameters

| System | Fitting equation | $\sigma$ | R |
|---|---|---|---|
| Methanol | $y = 166\,94x + 1120\,13$ | 5 06 | 0 993 |
| Ethanol | $y = 143\,76x + 1141\,63$ | 5 92 | 0 988 |
| 1-Propanol | $y = 81\,479x + 1190\,42$ | 2 88 | 0 991 |

The perusal of Figures 1–3 reveals good and fair agreement between the experimental and calculated sound velocities owing to the several assumptions and approximation made in the respective theories In all the three systems the linear fitting seems to be the best fit that indicates that the existing interactions are weak The IMR method is based on the ideality of the components [11] and hence this model seems to fail more for methanol system Further IMR model is more suitable for mixtures in which the components molecules are of same size FLT treats the molecules as rigid spheres [12] and hence it totally fails in all the present systems This reveals that the components of the binaries are highly involved in interactions are also able to form or deform their structures The validity of Rao's method demands the additivity of specific sound velocity [13] This can hold good only for ideal mixtures Thus the failure of Rao's method is again an indication that the system is not ideal though the interactions are weak

Of the four theories taken, NR seems to match closer with the experiment in all the systems Of course slight deviations in all the systems are found in the NR method also Such variations may be attributed to the fact that NR method requires the linear dependence

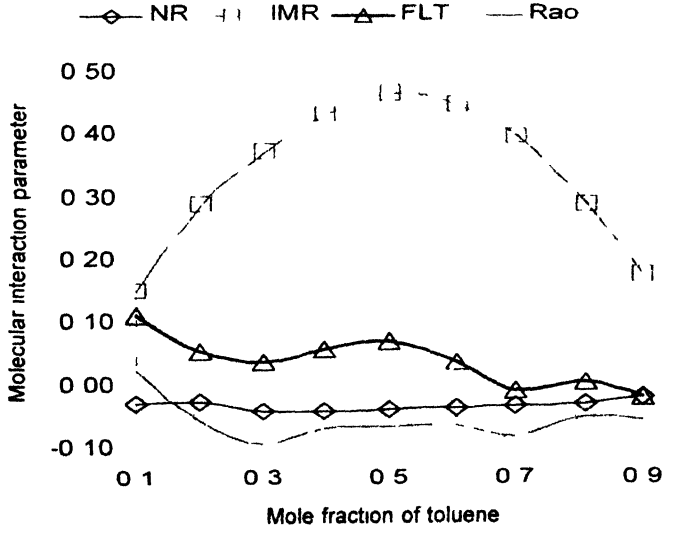


**Figure 4** Trend of molecular interaction parameter in methanol system

**Table 2** Percentage deviation of sound velocity values in $ms^{-1}$ and the Chi-square values in the binary mixtures at 303 K

| $x_1$ | *Toluene + Methanol* | | | | $x_1$ | *Toluene + Ethanol* | | | $x_1$ | *Toluene + 1-propanol* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NR | IMR | FLT | Rao | | NR | IMR | FLT | Rao | | NR | IMR | FLT | Rao |
| 0 1006 | −1 46 | 6 72 | 5 14 | 1 08 | 0 1006 | −1 17 | 2 72 | 1 01 | −1 88 | 0 1001 | −0 67 | 0 78 | −2 53 | −3 90 |
| 0 2012 | −1 44 | 11 90 | 2 58 | −2 98 | 0 2000 | −0 01 | 6 47 | 1 96 | −1 87 | 0 2001 | −0 60 | 1 85 | −3 42 | −4 87 |
| 0 3009 | −2 24 | 14 67 | 1 69 | −5 16 | 0 3001 | −0 64 | 7 68 | 2 01 | −2 22 | 0 3007 | −0 87 | 2 43 | −3 81 | −5 77 |
| 0 3981 | −2 21 | 16 45 | 2 75 | −3 76 | 0 4000 | −0 87 | 8 66 | 3 55 | −1 35 | 0 3987 | −1 32 | 2 36 | −3 99 | −5 73 |
| 0 5016 | −2 11 | 17 44 | 3 28 | −3 65 | 0 5005 | −1 09 | 8 93 | 2 99 | −1 96 | 0 4985 | −1 55 | 2 34 | −2 76 | −4 87 |
| 0 6052 | −1 89 | 16 89 | 1 69 | −3 50 | 0 6000 | −1 25 | 8 46 | 3 47 | −1 09 | 0 6006 | −1 65 | 2 09 | −1 84 | −3 86 |
| 0 7001 | −1 73 | 15 38 | −0 58 | −4 46 | 0 7000 | −1 27 | 7 43 | 2 92 | −0 95 | 0 6999 | −1 62 | 1 69 | −2 53 | −3 96 |
| 0 8095 | −1 59 | 11 85 | 0 04 | −2 69 | 0 8000 | −1 13 | 5 74 | 1 98 | −0 90 | 0 8076 | −1 47 | 1 02 | −2 81 | −3 54 |
| 0 9011 | −1 09 | 7 68 | −1 15 | −3 01 | 0 9005 | −0 63 | 3 51 | 2 21 | 0 03 | 0 9006 | −0 86 | 0 61 | −1 67 | −2 10 |
| $\chi^2$ | 0 31 | 21 95 | 0 65 | 1 19 | | 0 09 | 5 20 | 0 69 | 0 22 | | 0 15 | 0 34 | 0 83 | 1 87 |

of molar sound velocity on mole fraction [9], where as the whole model is mainly based on the excess molar volume of the components The extent of excess molar volume is again directly related to the strength of interactions in the system Thus all the remaining theories approaches good match with the increasing chain length of alcohol or reducing interactions The generated linear fitting equations also show a larger standard deviation (Table 1) with lower correlation coefficient for ethanol system but they are very acceptable for the other two systems This implies that the methanol and 1-propanol systems more or less obey the linear trend and hence they possess more ideal nature and the ethanol system is having more non ideality

This discussion reveals that NR method is best suited for non-ideal systems whereas the other methods are more suitable for less non-ideal systems Thus it is expected that among the molecular interaction parameter calculated using the various models, NR should show minimum values The inspection of Figures 4–6 reveals that it is fully as per the expectation The larger magnitude of molecular interaction parameter noticed for other models shows the failure of the suitability of the model to the present experiment

It is observed from Table 2 that the predictions based on percentage deviation and Chi-square tests are similar, however those of Chi-square test are evident and further they are

fully in line with the above predictions. Chi-square follows Chi-square distribution with ($n$ – 1) degrees of freedom. For a set of nine readings of the present investigations, it is noted that if the $\chi^2$ value is less than 1.653, the theoretical values are acceptable as having only 1% error. To accept 5% error, $\chi^2$ values may go up to 2 730.

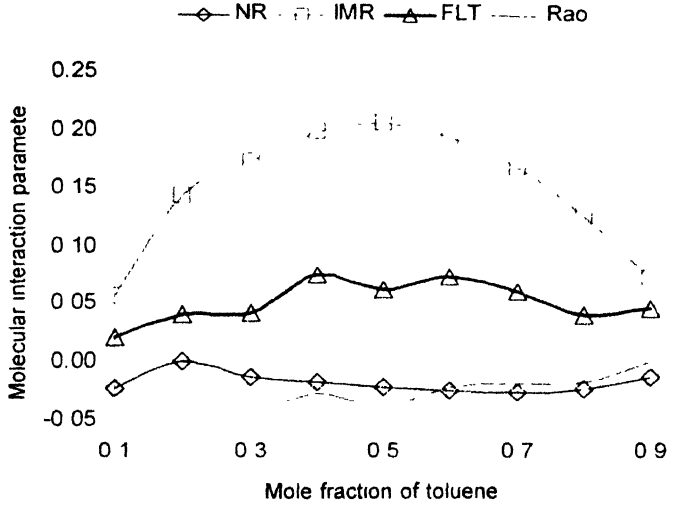


**Figure 5.** Trend of molecular interaction parameter in ethanol system

Among the four theories taken up in the present study, it is unanimously found that the prediction by NR method fit fairly well for all the binary mixtures considered In particular, FLT's prediction fails completely in toluene systems This may be attributed to the fact that toluene posses both electron donor and acceptor tendencies. Though the amino group in toluene is an inherent strong electron-donor, evidences can be found for

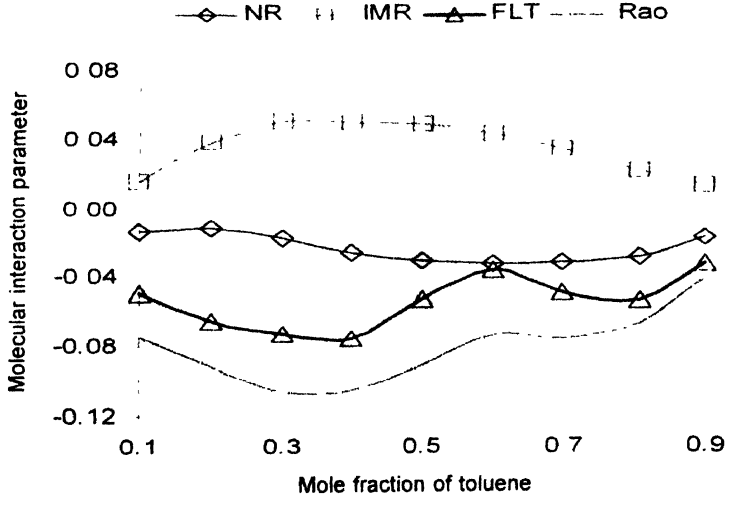


**Figure 6.** Trend of molecular interaction parameter in 1-propanol system

the H atoms in the $NH_2$ group to play the role of electron-acceptor centres [15]. A molecule having two contrary natures simultaneously cannot be rigid as assumed by FLT. The same is true for alcohol molecules also as they have one hydrophobic and hydrophilic contrary groups. As all the components violate the basic assumption of FLT, the theory for the present binaries totally failed.

As all the models are aiming at the sound velocity a positive value of the validation parameter, either molecular interaction parameter or the percentage deviation, indicates the existence of strong interactions. As NR is the only best suited model for the present systems existence of strong interactions is confirmed and the strength decreases as the chain length increases. This is reflected by the negative values of percentage deviation in 1-propanol system. Thus this analysis reconfirms the following conclusions and further goes one step ahead that it relates the strength of interaction and the chain length of alcohol.

## 5. Conclusions

(i) Among the four theories taken up, NR suits well for all the binary systems.

(ii) Components of the considered systems are not rigid and non-ideal.

(iii) Among the various binary mixtures considered, toluene + 1-propanol system is approaching ideality.

(iv) The strength of molecular interactions decreases as the chain length increases

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